

PII: S0043-1354(98)00234-6

SURFACTANT SELECTION FOR ENHANCING EX SITU SOIL WASHING

S. DESHPANDE¹, B.J. SHIAU¹, D. WADE¹, D.A. SABATINI*¹† and LH. HARWELL²

'School of Civil Engineering and Environmental Science, The Institute for Applied Surfactant Research, The University of Oklahoma, 202 West Boyd Street, Norman, OK 73019, U.S.A. and 'School of Chemical Engineering and Materials Science, The Institute for Applied Surfactant Research, The University of Oklahoma, Norman, OK 73019, U.S.A.

(First received September 1997; accepted in revised form May 1998)

Abstract—Ex situ soil washing is commonly used for treating contaminated soils by separating the most contaminated fraction of the soil for disposal. Surfactant-enhanced soil washing is being considered with increasing frequency to actually achieve soil-contaminant separation. In this research eight anionic and nonionic surfactants were evaluated for the enhanced soil washing of three different soils contaminated with petroleum hydrocarbons. Enhanced soil washing occurred at surfactant concentrations below and above the CMC indicating the occurrence of both soil rollup and solubilization mechanisms. In certain cases the lower CMC of nonionic surfactants made them attractive candidates while in other cases the lower sorption and higher solubilization potential of select anionic surfactants made them the preferred choice. Surfactant-induced foaming and turbidity are operating considerations that can also impact surfactant selection. When selecting a surfactant for a given soil-contaminants system we thus recommend evaluating both anionic and nonionic surfactants at concentrations below and above their CMC, and we suggest that the methodology we describe in this paper is a good approach for making the final surfactant selection. © 1998 Elsevier Science Ltd. All rights reserved

Key words-soil washing, surfactant, remediation

INTRODUCTION

In response to serious soil and ground water problems numerous advanced remediation technologies have been developed. Conventional pump-and-treat technologies are among the most widely used for the remediation of contaminated ground water (Palmer and Fish, 1992). However, experience has shown pump-and-treat to be ineffective at reducing contaminant levels. Soil washing (ex situ treatment of contaminated soils) also suffers from relatively poor soil-contaminant separation. Surfactant enhanced ground water remediation and soil washing are emerging technologies for enhancing the removal of organic contaminants from soil. Surfactants are particularly attractive for this process as they potentially have low toxicity and favorable biodegradability and can thus be more environmentally friendly than many organic-solvent based systems. However, surfactant selection guide-

LITERATURE REVIEW

Surfactants are amphiphilic molecules having two major components (moieties); a hydrophilic, or water soluble, head group, and a hydrophobic, or water insoluble, tail group. This dual nature causes surfactants to adsorb at interfaces thereby reducing the interfacial energies (Rosen, 1989). Depending on the surfactant head group they are classified as either anionic, cationic, nonionic, or zwitterionic (cationic and anionic groups).

At low concentrations surfactants exist solely as monomers. These monomers will accumulate at interfaces present in the system (e.g., air—water, oil—water, soil—water). As the interfacial areas are satisfied and the aqueous surfactant concentration increases the monomers aggregate to form micelles. The concentration at which micelles first begin to form is known as the critical micelle concentration (CMC).

Surfactant enhanced soil washing can result from two distinct mechanisms: one occurs below the critical micelle concentration (soil rollup mechanism) and the other occurs above the critical micelle concentration (solubilization). Surfactant monomers

lines are needed to aid in the implementation of surfactant-enhanced ex situ soil washing.

^{*}Address until July 15, 1998: Institute of Geologie, Lehrstuhl fur Angewandte Geologie, Sigwartstr. 10, 72076 Tubingen, Germany. [Tel.: +49-7071-2973061, Fax: +49-7071-5059, E-mail: sabatini@uni-tuebingen.de].

[†]Author to whom all correspondence should be addressed. [Tel.: +1-405-3254273; Fax: +1-405-3254217; E-mail: sabatini@mailhost.ecn.ou.edu].

are responsible for the soil rollup mechanism which occurs in two steps. In the first step surfactant monomers accumulate at the soil-contaminant and soil-water interfaces and increase the contact angle between the soil and the contaminant (i.e. change the wettability of the system). Surfactant molecules adsorbed on the surface of the contaminant cause a repulsion between the head group of the surfactant molecule and the soil particles, thereby promoting the separation of the contaminant from the soil particles. In the second step convective currents create agitation and abrasion which provides the energy necessary to create additional surface area of the oil phase and thus displace the oil from the soil. Both of these steps are necessary for the soil rollup mechanism to be significant (Rosen, 1989).

The second mechanism for enhanced soil washing is solubilization. Surfactant enhanced solubilization results from contaminant partitioning into the hydrophobic core of surfactant micelles. As the number of micelles in solution increases solubilization increases. Thus, concentrations well above the CMC are necessary for this enhancement to be significant. This mechanism has been widely studied in surfactant enhanced *in situ* soil washing.

While a substantial body of literature exists for surfactant enhanced ground water remediation (Abdul et al., 1990; Edwards et al., 1991; Rouse et al., 1993; Pennell et al., 1994; Sabatini et al., 1995), much less research has evaluated surfactant enhanced ex situ soil washing. Khodadoust and Wagner (1994) conducted in situ and ex situ soil washing studies using pentachlorophenol (PCP) contaminated soils. They used ethanol and acetone as their solvents and found that ethanol was a more effective cosolvent than acetone. Lower solvent flow rates were more effective at eluting the PCP, for the same solvent throughput, than higher flow rates suggesting that contaminant elution was rate limited by desorption kinetics.

Cosolvation is not without its drawbacks. The cosolvent can affect the soil matrix and has led to the formation of high permeability pathways (Khodadoust and Wagner, 1994). Cosolvents can also lead to biofouling in the subsurface. The solvents used can react with metals present in the soil and cause problems. Also, additional treatment facilities may be necessary for cosolvent—water separation (Khodadoust and Wagner, 1994).

Waste-Tech services (Millet and Trost, 1992) and Biotrol (Stinson, 1992) conducted pilot plant studies of *ex situ* soil washing. In these studies size separation was the main process utilized, with bioreactors being used in a few cases. These pilot plant studies showed *ex situ* soil washing to be a viable alternative to *in situ* remediation.

Ghea Associates (Gotlieb *et al.*, 1993) used surfactants for *ex situ* soil washing studies. They treated soils contaminated with coal tar, PCBs, hydrocarbons, chlorinated hydrocarbons etc. Their

research included a pilot plant study. Contaminant removal approached 99% in many cases. The process cost was estimated at \$50–80 per ton of soil. This compared favorably to other separation processes whose costs ranged from \$90 to \$200 per ton.

Surfactant enhanced *ex situ* soil washing can offer the convenience, efficiency and economy desirable for innovative and alternative soil washing technologies. Guidance in selecting surfactants to be evaluated in *ex situ* soil washing is important for the soil remediation industry; such is the focus of this study.

OBJECTIVES

The overall objective of this research is to provide guidance in selecting surfactants for enhanced *ex situ* soil washing. Specific objectives of this research include:

- (1) Evaluate the occurrence of soil rollup (sub-CMC) and solubilization (supra-CMC) mechanisms in *ex situ* soil washing.
- (2) Quantitatively evaluate soil—contaminant—surfactant interactions that impact the efficiency of *ex situ* soil washing (e.g. solubilization, sorption).
- (3) Qualitatively evaluate additional surfactant properties that will affect the soil washing process (e.g. foaming, phase separation, precipitation), and
- (4) based on the above results provide guidelines for evaluating and selecting surfactants for a given soil washing activity.

This research evaluated soil washing of one contaminant type (petroleum hydrocarbons) with three soils (having varying clay and organic content) and a range of surfactants. While the results may be specific to petroleum hydrocarbons the methodology used can be easily applied to additional contaminant types (as well as for petroleum hydrocarbons with other soils and surfactants).

EXPERIMENTAL MATERIALS AND METHODS

Three soils were chosen for evaluation in this research based on their varying physicochemical properties (e.g., grain size distribution, clay content and organic content). The soils chosen for this study and their properties are listed in Table 1. The first soil studied was Canadian River Alluvium (CRA), which was artificially contaminated with petroleum hydrocarbon contaminants. The other two media were contaminated soils obtained from Hill Air Force Base, UT and a gasoline station in Ardmore, OK. The soils from field contamination sites have been exposed to petroleum hydrocarbon contamination for extended periods of time (one to several decades).

The surfactants studied in this research were selected to include both nonionic and anionic surfactants as well as surfactants having USFDA direct food additive status and surfactants that have previously been shown to minimize sorption and precipitation losses. The surfactants, along with their relevant properties, are listed in Table 2. Nonionic surfactants evaluated include: polyethoxylated sorbitol esters (T-Maz 80, T-Maz 20) obtained from PPG/Mazer, alkyl phenol ethoxylates (CA 620) obtained from Rhone-Poulenc, and TerraSurf 80 from Dow Europe.

Table 1. Physical characteristics of the soils used in this study

| Parameter | Canadian river alluvium (CRA) | Hill AFB (HAFB) soil | Ardmore soil |
|---|-------------------------------|----------------------|--------------|
| | Composition (| (%) | |
| Coarse sand | 21.9 | 32 | 40 |
| Fine sand | 50.1 | 64 | |
| Silt | 22.4 | | 30 |
| Clay | 5.6 | 4.6 | 30 |
| Organic carbon content $(f_{oc})^a$ | 0.0007 | 0.008 | 0.005 |
| pH ^a | 8.2 | 8.2 | 8.4 |
| Cation exchange capacity (meq/100 g) ^a | 2.5 | 19.3 | 23.1 |
| Bulk density (g/cm ³) ^a | 1.60 | 1.40 | 1.30 |

^aMeasurements by Harris Laboratories

Anionic surfactants screened include: alkylated diphenyloxide disulfonates (Dowfax 8390) obtained from Dow Chemicals, alkylbenzene monosulfonates (sodium dodecyl benzene sulfonate) obtained from Aldrich Chemicals, alkyl sulfates (sodium dodecyl sulfate) obtained from Fisher Scientific, and alkyl ether sulfates (Steol 330) obtained from Stephan Company. The surfactants were used as received. These surfactants have been well characterized and studied in our laboratories (Rouse et al., 1993, 1996; Shiau et al., 1994, 1995, 1996).

The research was divided into stages corresponding to the three soil types evaluated. In preliminary studies (the first stage), CRA was contaminated with phenanthrene (a representative polycyclic aromatic hydrocarbon) and decane (a representative long chain alkane); all surfactants were evaluated for this soil (Table 2). Batch studies were conducted over a range of surfactant concentrations while the "extraction" efficiency was determined (the quantity of contaminant extracted by each surfactant per unit of surfactant).

In the second stage HAFB soil was treated. This soil has been contaminated for several decades and is thus more representative of most sites than artificially contaminated soil. In the third stage, soil washing experiments were conducted on soil obtained from a gasoline station in Ardmore, OK.

The most significant measurement in these studies was the contaminant concentration in the wash solution, which is the basis for determining the enhancement in extraction efficiency as a function of surfactant concentration. Other important interactions include the soil-surfactant interaction (sorption), surfactant precipitation, phase separation and foaming. Based on these results guidelines are provided for surfactant selection based on maximum contaminant extraction, minimum surfactant losses due to sorption, precipitation and foaming, and lack of surfactant phase separation.

Select soil samples were air dried for 24 h followed by oven drying at 105°C for 12 h. The difference between the initial and final weights is the moisture content of the soil. Size classification was achieved by sieving into gravel, medium and coarse sand, fine sand and silt + clay fractions. The pH, organic content, bulk density, and cation exchange capacity of the soil were determined by a professional soil testing laboratory (Harris Laboratories).

Batch soil washing studies were conducted by placing a constant ratio of soil to surfactant solution (3 g/15 ml) in a 40 ml EPA vial (Fisher Scientific) at room temperature (~23°C). The vials were shaken for 30 min on a wrist action shaker and then allowed to settle for 24 h. The solution was then separated by centrifugation and aqueous petroleum hydrocarbons concentration were measured by gas chromatography. The surfactant concentration was varied by two orders of magnitude from below the CMC to above the CMC (0.25 times, 4 times and 25 times the CMC). These surfactant concentrations were used to evaluate the occurrence of soil rollup (below the CMC) and solubilization (above the CMC) mechanisms. Since surfactant CMCs vary dramatically for anionic and nonionic surfactants (as much as two orders of magnitude, see Table 2), and since surfactant costs will correspond to mass of surfactant purchased, soil washing results will also be discussed in terms of absolute surfactant concentrations.

The initial petroleum hydrocarbon contamination in the soil was measured by extracting a sample of the contaminated soil with methylene chloride with the extraction solutions quantified by gas chromatography (according to

Table 2. Properties of surfactants used in this study

| Surfactant | Chemical structure | Activity (%) | Molecular weight | CMC mM (mg/L) |
|---------------|--|--------------|------------------|-------------------------|
| SDS | sodium dodecyl sulfate ^f | 100 | 288 | 8.4 (2420) ^b |
| | sodium dodecyl benzene | 100 | 324 | * * |
| SDBS | sulfonate | | | 1.19 (390) ^b |
| | sodium lauryl POE(3) | 27.5 | 442 | (-1.7) |
| Steol CS-330 | sulfateg | | | 3.3 (1460) ^c |
| | sodium n-hexadecyl | 35.9 | 642 | |
| Dowfax 8390 | diphenyloxide disulfonate ^g | | | 6.3 (4040) ^c |
| | POE ^a (20) sorbitan | 100 | 1227 | |
| T-Maz 20 | monolaurate ^f | | | $0.049 (60)^{d}$ |
| | POE ^a (20) sorbitan | 100 | 1308 | (, |
| T-Maz 80 | monooleate ^f | | | $0.01 (13)^{d}$ |
| | octylphenoxy $POE(x)$ | 100 | 620 | (11) |
| Igepal CA-620 | ethanol | | | 0.1 (62) |
| TerraSurf 80 | | 100 | 595 | $0.05 (30)^{e}$ |

Number in parentheses indicate number of ethylene oxide (EO) groups.

^aPOE = Polyethoxylated.

^bMukerjee and Mysels (1971).

^cRouse *et al.*, 1993. ^dShiau *et al.*, 1995.

eProvided by Dow Europe.

fUSFDA Direct Food Additive Status.

g"High performance" surfactants (reduced sorption and precipitation tendencies, Rouse et al., 1993, 1996).

Vandegrift and Kampbell, 1988). In order to evaluate data reproducibility, a second set of solubilization studies were conducted using Dowfax, Steol and T-Maz 80 surfactants with decane-contaminated CRA and the HAFB soil; duplicate results were virtually identical, verifying data reproducibility.

Sorption studies were conducted in 40 ml EPA vials using the same soil/surfactant ratio (3.0 g/15 ml) using the same range of initial surfactant concentrations as above. The surfactant/soil mixture was shaken for 30 min, equilibrated and the final surfactant concentration measured. The same batch method was also used to evaluate the turbidity and phase separation characteristics of the wash solution. The glassware used in this study was washed thoroughly with Alconox detergent, then cleaned with Nochromix solution, rinsed well with D.I. water and finally dried in an oven at 100°C. Gravimetric measurements were conducted on a Sartorius balance (0.0001 g).

The Ross–Miles method was used to study surfactant foaming properties (Rosen, 1989). In the Ross–Miles method, 200 ml of a surfactant solution is placed in a pipette of specified dimensions (2.9 mm I.D. orifice) and then allowed to fall 90 cm onto 50 ml of the same solution in a cylindrical vessel. The height of the foam produced in the cylindrical vessel is read immediately after all the solution has run out of the pipette and a subsequent reading is taken after 5 min (Rosen, 1989). Since foaming is generally maximum at the CMC surfactant concentration were evaluated below and above the CMC (0.25, 4 and 25 times the CMC).

Hydrocarbon concentrations were measured using a GC/Static Headspace technique. To account for surfactant-reduced sample volatility all samples and standards were normalized to a common surfactant concentration thereby equalizing the effect. A Shimadzu 17A gas chromatograph was used with a Tekmar 7000 headspace autosampler and a Tekmar 7050 carrousel. The injector and detector temperatures were 250 and 280°C, respectively. The column temperature was ramped at the rate of 8°/min from 40 to 230°C. A Varian Star Chromatography workstation was used for data collection. A J and W scientific DB-5, 30 meter long column with 0.53 mm I.D. and 1.5 µm film thickness was used. The reagents used included SYBRON-Barnstead double deionized water and organic analytes of 97% purity or higher.

Surfactant concentrations were analyzed using high pressure liquid chromatography (HPLC). A Beckman 110B solvent delivery module with a manual 210A sample injection valve was used as the HPLC system. The UV detector used was either a Beckman 166 programmable module or a Waters 486 tunable absorbance detector. An Alltech 320 conductivity detector was used whenever the parameter to be measured was conductivity. An Alltech reversed-phase nucleosil C18, 5 $\mu \rm m$, 150 × 4.6 mm column was used with Alltech All-Guard cartridges as pre-columns. The mobile phase used was typically an 80% methanol (HPLC grade)/water solution.

Turbidity tests were conducted using a HACH turbidimeter (Model 2100A). Calibration standards were as provided by the company. Turbidity vials (25 ml) were used in the turbidimeter were filled with the supernatant surfactant solutions obtained after soil washing and the turbidity readings were noted. In many cases several dilutions were required to obtain readings.

Surfactant phase separation was studied using a Bausch and Lomb microscope with a polarized filter. A drop of the wash solution was placed on a slide and observed under the microscope. The potential for liquid crystalline phases was observed through interchange with an ordinary light and a polarized light source via different reflection patterns (Shiau *et al.*, 1996).

RESULTS AND DISCUSSION

Contaminant extraction studies

Contaminant extraction studies were conducted on three soils (CRA, HAFB, and Ardmore, see Table 1) using eight surfactants (Table 2). These studies were conducted to determine the contaminant extracted for each surfactant and contaminated soil and as a function of surfactant concentration.

Soil washing results for phenanthrene-contaminated CRA media are presented in Fig. 1. Phenanthrene concentrations (mg/L) have been plotted as a function of the surfactant concentration relative to the CMC to highlight the occurrence of soil rollup (sub-CMC) and solubilization (supra-CMC) mechanisms. The water only concentrations were 1.2 mg/L which was near the detection limit of 0.5 mg/L. The data in Fig. 1 demonstrate that surfactant-enhanced results are one to two orders of magnitude greater than water only, and that surfactant-enhanced concentrations occurred both below and above the CMC. These observations demonstrate the efficacy of surfactant-enhanced soil washing and suggest that surfactant-induced rollup and solubilization mechanisms are both active in the extraction process. The fact that sub-CMC surfactant concentrations enhanced soil washing by as much as an order of magnitude is encouraging as these lower surfactant concentrations improve the economic attractiveness of this technology. While the soil washing further improved at higher surfactant concentrations (by as much as another order of magnitude) this improvement may be offset by the higher surfactant costs associated with these much higher concentrations (25 vs 0.25 times the

In Fig. 2 and 3 soil washing results are presented for the HAFB as a function of absolute surfactant concentration and surfactant concentrations normalized to CMC, respectively. Figure 2 emphasizes the results as a function of surfactant concentration (and thus surfactant cost) while Fig. 3 allows investigation of the sub- and supra-CMC results while also making it easier to see trends between surfactant series. From Fig. 2 it is observed that surfactant-enhanced contaminant concentrations are two to three orders of magnitude higher than water alone. The data in Fig. 3 illustrate that for select surfactants this enhancement occurred both below and above the CMC while for other surfactants no further enhancement was observed above the CMC (as discussed further below).

Table 3 documents the ratio of contaminant concentrations at two surfactant levels; 25 and 0.25 times the CMC. When surfactant solubilization enhances soil washing this ratio will be greater than one (i.e. contaminant concentrations are greater at 25 times the CMC than at 0.25 times the CMC due to solubilization). As values of this ratio approach

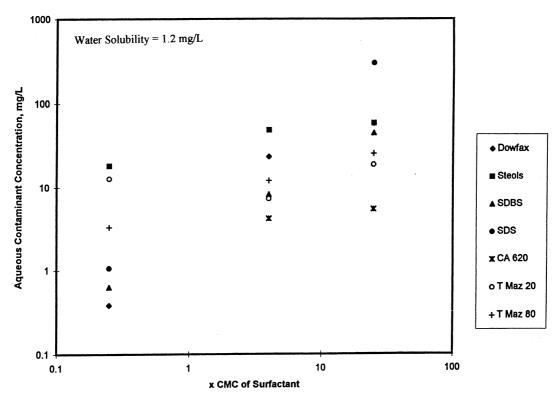


Fig. 1. Extraction studies of phenanthrene from CRA as a function of surfactant and concentration (relative to CMC).

one the impact of surfactant solubilization is minimal. Thus this ratio provides a quantitative measure of the supra- to sub-CMC results shown in Figs 2 and 3. From Table 3 it is observed that for the HAFB soil contaminant extraction efficiencies improved above the CMC for the anionic surfactants (first four surfactants in Table 3) while contaminant extraction efficiencies showed no change for supra-CMC nonionic surfactant concentrations (second four surfactants in Table 3). It was hypothesized that significant sorption of the nonionic surfactants negated their solubilization potential; this observation was corroborated when final surfactant concentrations were analyzed and found to be below the CMC of the nonionic surfactants. Visual and microscopic observations showed no visible phase separation or precipitation of the surfactants in the wash solutions while sorption studies showed much greater sorption of the nonionic surfactants vs the anionic surfactants (since surfactant concentrations were below the CMC linear distribution coefficients were quantified; these values were found to be $> 20 \text{ cm}^3/\text{g}$ and $< 1.0 \text{ cm}^3/\text{g}$ for nonionic and anionic surfactants, respectively).

While discussing the fundamental occurrence of soil rollup and solubilization mechanisms we have looked at surfactant concentrations normalized to the CMC. However, normalizing surfactant concentrations in this manner hides the fact that nonionic surfactants have much lower CMCs which may be

a critical factor in evaluating the economics of these systems. Thus, when considering the overall system efficiency and economics we focus on actual surfactant concentrations as shown in Fig. 2. For example, if the soil rollup mechanism is sufficient to achieve the desired soil washing results at 0.25 times the CMC then nonionic surfactants may well be the preferred choice because of the lower amount of surfactant required (3 mg/L for T Maz 80 vs 600 mg/L for SDS). At the same time, if the nonionic surfactant is significantly sorbed and this sorption negates the soil washing efficiency then this difference may be reduced or even reversed for a given system.

In Fig. 2 we see that 10 to 100 mg/L of the nonionic surfactants enhance the contaminant solubility by one to two orders of magnitude while anionic surfactant concentrations of 100 to 1000 mg/L are necessary to realize similar results. If this level of enhancement is sufficient then the nonionic surfactants will be economically preferred for this system (i.e., we need to purchase 10-100 times less of the nonionic surfactant). At the same time with increasing concentration anionic surfactants can achieve an order of magnitude greater enhancement in contaminant concentrations than possible with the nonionic surfactants — the relative economics will determine the attractiveness of this approach. Thus, while fundamental considerations can help select surfactants for screening purposes economic con-

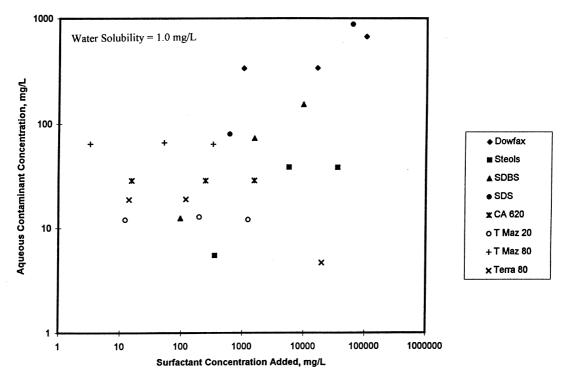


Fig. 2. Extraction studies from HAFB soil as a function of surfactant and concentration.

siderations will dictate the optimal surfactant system

For the soil obtained from a gasoline station in Ardmore, OK, the nonionic and anionic surfactants

extracted similar amounts of contaminant (from one to two orders of magnitude higher than water alone — Fig. 4). Except for Dowfax 8390 none of the surfactants showed an increase in the amount of

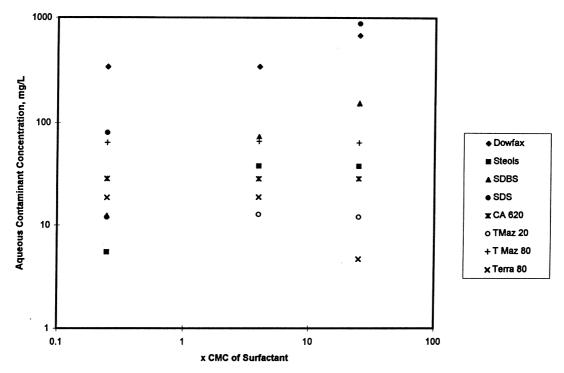


Fig. 3. extraction studies from HAFB soil as a function of surfactant and concentration (relative to CMC)

Table 3. Ratio of contaminant concentration at 25 and 0.25 times the CMC for eight surfactants and two site-contaminated soils

| Surfactant/soil | HAFB soil | Ardmore soil |
|-----------------|-----------|--------------|
| Dowfax 8390 | 2.0 | 3.6 |
| Steol 330 | 6.9 | 1.2 |
| SDBS | 12 | 0.90 |
| SDS | 11 | 0.99 |
| T Maz 20 | 1.0 | 0.97 |
| T Maz 80 | 1.0 | 0.97 |
| CA 620 | 1.0 | 1.0 |
| Terra Surf 80 | 0.24 | 1.0 |

contaminant extracted with increase in surfactant concentration from below to above the CMC (Fig. 4 and Table 3). Visual observation of the wash solutions showed no phase separation or precipitation occurred. The Ardmore soil has the highest clay content (Table 1) and hence produced the most turbid wash solutions (as discussed further below). The lower sorption of nonionic surfactants on the Ardmore soil $(\sim 10 \text{ cm}^3/\text{g} \text{ vs} > 20 \text{ cm}^3/\text{g} \text{ for the}$ HAFB soil) apparently caused the nonionic and anionic surfactants to perform equally well for this system (Fig. 4 and Table 3). While SDS did achieve slightly higher contaminant concentrations it is very unlikely that this slight enhancement will justify the two orders of magnitude higher surfactant concentrations required. These results illustrate the importance of evaluating a suite of surfactants for each

soil and contaminant. While fundamental considerations can guide the selection of surfactants and concentrations for testing, soil and contaminant heterogeneities require experimental testing for final system selection.

Foaming and turbidity tests

Foaming tests were conducted for all the surfactants and their respective concentrations using the Ross-Miles apparatus (Rosen, 1989). The results are presented as bar graphs in Fig. 5. As expected, the anionic surfactants showed a greater tendency to foam than the nonionic surfactants (Rosen, 1989). The nonionic surfactants have a larger surface area per molecule and do not have highly charged surface films in their foams and thus generally produce less foam. Although foaming may not affect the solubilization performance of the surfactant to a significant extent, formation of large amounts of foam will make handling the surfactant solution difficult. Also solutions that foam heavily may not be accepted into discharge waste streams due to regulatory restrictions.

Turbidity tests were conducted for the CRA, HAFB and Ardmore, OK soils. The tests indicate that turbidity was highest in the case of Ardmore soil (1,000–10,000 NTU) vs the other two soils (NTU values less than 1,000). This was expected as the clay content and the cation exchange capacity

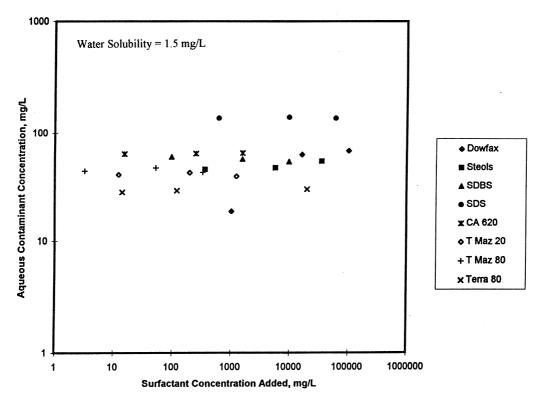


Fig. 4. Extraction studies from Ardmore soil as a function of surfactant and concentration.

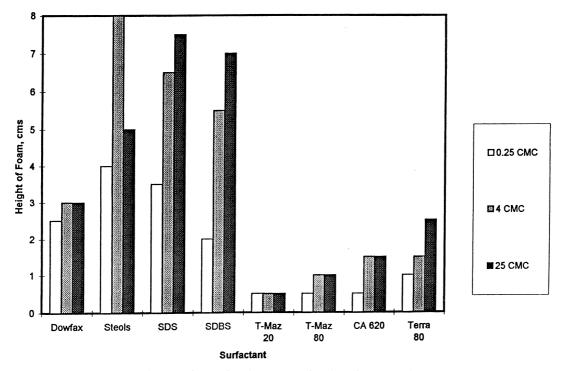


Fig. 5. Surfactant foaming test as a function of concentration.

of this soil are higher than the Hill AFB soil or the CRA soil (Table 1). The Hill AFB soil showed more turbidity in its wash solutions than the CRA soil, in spite of having similar clay contents. This was expected as the cation exchange capacity of the

HAFB soil is greater than that of the CRA soil (Table 1). In the case of Hill AFB soil and the CRA soil, where clay content was not very high, the nonionic surfactant solutions were clearly less turbid than the anionic surfactant solutions (Fig. 6).

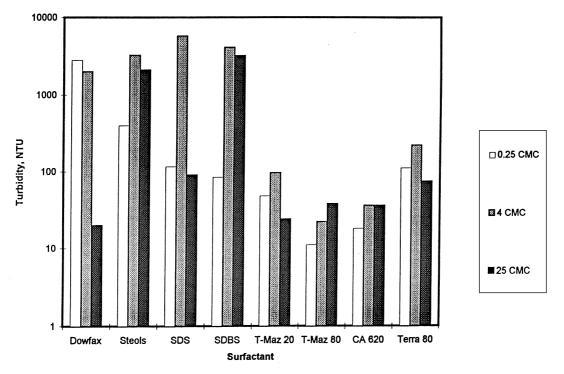


Fig. 6. Turbidity tests for HAFB soil as a function of surfactant and concentration.

In both the foaming and turbidity studies surfactant concentrations were expressed normalized to the surfactant CMC. While the actual surfactant concentrations may vary dramatically (as much as two orders of magnitude for nonionic and anionic surfactants evaluated here) we used these concentrations because they are the likely levels at which the respective surfactants will be used. In addition these concentrations allowed examination of the processes being studied. Obviously these tests should be repeated for a given surfactant and concentration to be used in a particular soil washing study.

Guidelines for surfactant screening

In this section we will summarize some of the main conclusions from this research and provide some surfactant screening guidelines for ex situ soil washing. These studies have shown that both soil rollup and solubilization mechanisms were active during soil washing, with the magnitude of each effect being a function of the extent of surfactant sorption and the soil grain size distribution. For a given soil-contaminant system if the soil rollup mechanism is significant and produces desirable results then the lower CMC of nonionic surfactants may render them economically preferred. However, when the anionic surfactants experience much less sorption and thus result in higher soil rollup or solubilization this may dominate the efficiency of the soil washing process and thus surfactant selection (in this study the Dowfax and Steols surfactants are especially resistant to sorption and precipitation losses — Rouse et al., 1993, 1996). For some soil-contaminant systems the surfactants may perform similarly irrespective of the surfactant or concentration. In this case the lower CMC of nonionic surfactants may again be attractive. Surfactant selection must also consider operating factors such as turbidity and foam generation. Obviously economic considerations will dictate the preferred surfactant system.

The fact that the surfactants behaved differently for the three soil-contaminant systems illustrates the importance of bench-scale testing when selecting a surfactant for a given soil-contaminant system. We suggest that both anionic and nonionic surfactants be included in this screening and that they should be evaluated at concentrations below and well above their CMC (0.25 and at least 10 to 25 times the CMC). We selected the surfactants in this research based on their likelihood to enhance the soil washing efficiency while minimizing surfactant losses. Thus we suggest these surfactants as good candidates for screening for a given soil-contaminant system. We also suggest that our methodology be used for screening surfactants for soil washing efficiency and operational considerations (phase separation during soil washing, and separate foaming and turbidity tests) for a given application. As additional data becomes available (based on additional soil-contaminant systems and with additional surfactants) these results can be integrated with our data and additional guidelines developed.

Acknowledgements—Although the research in this article was funded by the United States Environmental Protection Agency (Edison, NJ) through the Northeast Hazardous Substances Research Center (NJIT), it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency, and no official endorsement should be inferred. The authors wish to thank Mr. Michael Borst (USEPA) and Dr. Richard Magee (NJIT) for their insightful comments and helpful suggestions during the course of this research. The authors wish to acknowledge the helpful review comments of the anonymous reviewers. This paper was revised while the corresponding author was a Senior Fulbright Scholar in the Lehrstuhl für Angewandte Geologie at the Universität Tübingen in Tübingen, Germany.

REFERENCES

Abdul A. S., Gibson T. L. and Rai D. N. (1990) Selection of surfactants for the removal of petroleum products from shallow sandy aquifers. *Ground Water* **28**(6), 920–926.

Edwards D. A., Luthy R. G. and Liu Z. (1991) Solubilization of polycyclic hydrocarbons in micellar nonionic surfactant solutions. *Environmental Science and Technology* **25**(1), 127–133.

Gotlieb I., Bozzelli J. W. and Gotlieb E. (1993) Soil and water decontamination by extraction with surfactants. *Separation Science and Technology* **28**(1–3), 793–804.

Khodadoust A. P. and Wagner J. A. (1994) Solvent washing of PCP contaminated soils with anaerobic treatment of wash fluids. *Water Environment Research* **66**(5), 692–697.

Mukerjee P. and Mysels K. J. (1971). Critical Micelle Concentrations of Aqueous Surfactant Systems. NSRDS-NBS 36, US Department of Commerce, Washington, DC

Millet P. R. and Trost P. B. (1992) "Design and Field Demonstration of a Mobile 50 Ton per Day Soil Washing Facility for Cleaning Petroleum Hydrocarbon-Contaminated Soils." presented at the I and EC Special Symposium American Chemical Society, Atlanta, September 1992, 369–372.

Palmer C. D. and Fish W. (1992) Chemical enhancements to pump-and-treat remediation. *Ground Water Issue* **January**, 1–19.

Pennell K. D., Jin M., Abriola L. M. and Pope G. A. (1994) Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene. *Journal of Contaminant Hydrology* **16**(1), 35–53.

Rosen M. J. (1989) Surfactants and Interfacial Phenomena. John Wiley and Sons, Inc., New York.

Rouse J. D., Sabatini D. A. and Harwell J. H. (1993)
Minimizing surfactant losses using twin-head anionic surfactants in subsurface remediation. *Environmental Science and Technology* 27(10), 2072–2078.
Rouse J. D., Sabatini D. A., Brown R. E. and Harwell J.

Rouse J. D., Sabatini D. A., Brown R. E. and Harwell J. H. (1996) Evaluation of ethoxylated alkylsulfate surfactants for use in subsurface remediation. Water Environment Research 68(2), 162–168.

Sabatini D. A., Knox R. C. and Harwell J. H. eds (1995) Surfactant Enhanced Subsurface Remediation: Emerging Technologies. ACS Symposium Series 594, American Chemical Society, Washington, DC.

- Shiau B. J., Sabatini D. A. and Harwell J. H. (1994) Solubilization and microemulsification of chlorinated solvents using direct food additive (edible) surfactants.
- Ground Water 32(4), 561–569.

 Shiau B. J., Sabatini D. A. and Harwell J. H. (1995)

 Properties of food grade surfactants affecting subsurface remediation of chlorinated solvents. *Environmental Science and Technology* **29**(12), 2929–2935.

 Shiau B. J., Sabatini D. A. and Harwell J. H. (1996) Properties of food grade surfactants affecting subsurface
- remediation of chlorinated solvents. Environmental
- Science and Technology **31**(1), 97–103.

 Stinson M. K. (1992) EPA Evaluation of the BioTrol Soil Washing Process, presented at the I and EC Special Symposium American Chemical Society, Atlanta, September 1992, 378–381.
- Vandegrift S. and Kampbell D. (1988) Gas chromatographic determination of aviation gasoline and JP-4 jet fuel in subsurface core samples. *Journal of Chromatographic Science* **26**, 566–569.